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Negative tone molecular resists using cationic polymerization: Comparison of epoxide and oxetane functional groups

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Two molecular resists with a common molecular glass core were synthesized and characterized to compare the differences between epoxide (oxirane) and oxetane functional groups for use in high resolution negative tone molecular resists. Both resists are able to obtain at least 50 nm half-pitch at a sensitivity of $75 \mu\text{C}/\text{cm}^2$ under 100 keV electron-beam lithography. Due to differences in the kinetics of the cationic polymerization of epoxides as compared to oxetanes, the epoxide functionalized resist (2-Ep) was able to obtain sub-25-nm half-pitch resolution with good line edge roughness (LER) of 2.9 nm (3σ) while the oxetane resist (2-Ox) was limited to 50 nm half-pitch resolution and exhibited higher LER (3σ) of 10.0 nm. The polymerization of the oxetane functional group has slow initiation and fast propagation which leads to reduced performance in 2-Ox as compared to 2-Ep. While oxetane functionalized molecular resists can obtain reasonably good imaging performance, epoxide functional groups show more promise for use in next generation negative tone resists that have a good combination of resolution, sensitivity, and LER. © 2009 American Vacuum Society. [DOI: 10.1116/1.3264672]

I. INTRODUCTION

There is an ever increasing need to obtain photoresists that can simultaneously obtain good resolution, line edge roughness (LER), and sensitivity for high resolution lithography using both current (i.e., 193 nm exposure) and future [i.e., 13.5 nm, extreme ultraviolet (EUV)] optical lithography. In conventional chemically amplified resists (CARs), these three parameters cannot be simultaneously optimized for a given resist material/formulation.¹ Any two of these parameters can be improved, but only at the expense of decreased performance in the third. This principle in CARs has come to be known as the resolution, line edge roughness, sensitivity (RLS) tradeoff.² Nonchemically amplified resists (non-CARs) can likely be considered an extreme case of this. They have very high resolution and good LER,^{3,4} but significantly worse sensitivity than would be considered useful for modern high volume sub-0.25- μm commercial semiconductor fabrication. One of the main reasons that CARs have such difficulty obtaining all three parameters is due to photoacid diffusion. By increasing photoacid diffusion, sensitivity is improved, but resolution is lost due to diffusion of the photoacid outside of the nominally exposed areas.⁵ The effect of increasing photoacid diffusion on LER is even more complex

and may either be improved or made worse depending on the material system and processing conditions used. Reducing diffusion leads to improved resolution but at the loss sensitivity, and can potentially lead to increased LER. To overcome these problems, radical new resist designs must be investigated.^{6,7}

One such approach for overcoming the RLS tradeoff is the use of cationic polymerization, such as epoxide polymerization, to carry out solubility switching by an increase in molecular weight instead of the acid catalyzed deprotection of protecting groups used in current positive tone CARs. In cationic polymerization, the photoacid protonates the ring which activates it for attack by another ring which is the initiation step.⁸ Once the initiation step occurs, the original photoacid is gone and cannot be generated without a chain-transfer-type reaction with an alcohol, acid, or water. This property allows high resolution in epoxide molecular resists because diffusion of the photoacid is not important. The photoacid in these systems is immediately consumed by ring protonation and initiation. The photoacid is no longer the active species in the resist, and instead it is the cationic active site on the chain end that is carrying out further reactions. This approach allows for several potential advantages over current CAR designs. Since the final film is a highly cross-linked film, it should have superior mechanical strength compared to non-cross-linked positive tone resists

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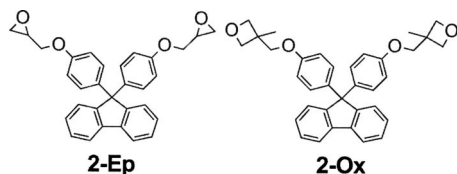


FIG. 1. Chemical structures of 2-Ep and 2-Ox.

which would result in improvements in pattern collapse behavior. These resists should also have little or no outgassing as compared to many conventional positive tone resists because ring-opening polymerization is a zero mass loss process. Another important potential advantage of this type of approach is the fact that there is effectively an intrinsic diffusion control due to the fact that the cationic active site is attached to a growing polymer chain or network. As the polymerization proceeds, the rate and further spatial length of propagation of polymerization from the active site should be reduced as well. One of the most commonly known resists of this type is SU-8 which has shown isolated line resolution down to 24 nm (Refs. 9–11) under electron-beam (e-beam) patterning which confirms the resolution capability in these types of materials. However, it has been shown that the resolution of SU-8 is limited in dense features due to swelling.¹²

Molecular glass photoresists (molecular resists) have many favorable properties such as the ability to create monodisperse resists with very well defined structures and functionality through precisely controlled synthesis and purification. Their properties and structures can be systematically varied to investigate subtle structure-property relationship in such resist systems. Molecular resists have also shown themselves to be an excellent platform for negative tone resists based on cationic polymerization for a number of reasons that will be discussed later. Molecular resists based on cross-linked fullerenes have shown excellent results under e-beam imaging,¹³⁻¹⁷ and a few other reports of cross-linking calixarene resists have also shown good performance.¹⁸⁻²⁰ Our group has designed several of these resists²¹⁻²³ based on polyphenols whose structure and functionality have been systematically varied. These resists have shown sub-25-nm resolution, sensitivity as low as 20 $\mu\text{C}/\text{cm}^2$ at 100 keV, and very low LER (3σ) values of 2.3 nm in multiple systems. Despite the excellent performance of these materials, their contrast performance could still be enhanced. It is reported that oxetanes have much higher polymerization propagation rates than epoxides²⁴ (oxiranes) which could potentially lead to improved contrast. To systematically and carefully compare the difference between epoxides and oxetanes as functional groups for negative tone molecular resists based on cationic polymerization, two compounds that were as identical in structure and properties as possible were synthesized and characterized in this work, with the only major difference in the two materials being the polymerizable group. Figure 1 shows the chemical structures of these two compounds: (1) 2-Ep, the epoxide functionalized molecular resist, and (2) 2-Ox, the oxetane functionalized molecular resist.

II. EXPERIMENT

All reagents and solvents used were purchased from either Sigma-Aldrich, TCI America, or Alfa-Aesar and used as received. Triphenylsulfonium hexafluoroantimonate (SbF_6) photoacid generator was purchased from Midori Kagaku Co., Ltd. A Varian Mercury Vx 300 was used to collect NMR. Deep ultraviolet (DUV) exposures were done using an Oriel Instruments 500 W Hg–Xe arc lamp with a 248 nm bandpass filter. Film thicknesses were measured using an M-2000 spectroscopic ellipsometer (J.A. Woolam, Inc.) over the wavelengths of 350–1000 nm using a Cauchy layer to model the resist film. E-beam lithography was done using a JEOL JBX-9300FS electron-beam lithography system with 100 keV acceleration voltage, 2 nA current, and 10 nm single-pixel shot pitch. Resolution tests were done on resist films coated onto 46 nm thick silicon nitride membrane windows.²⁵ The patterns produced by e-beam lithography were imaged using a LEO 1530 thermally assisted field emission scanning electron microscope (SEM) with 3 keV acceleration voltage. Critical dimension measurements and the whole spatial-frequency 3σ LER and 3σ line width roughness (LWR) spectra of the resist pattern were averaged from ten different line-space patterns with an inspection length of 1 μm using a custom designed MATLAB program.

Synthesis of 2-Ep is described elsewhere,²³ but the synthesis of 2-Ox is new and is described here. Sodium hydroxide (1.058 g, 26.5 mmol) and 9,9-bis(4-hydroxyphenyl)fluorene (3.00 g, 8.6 mmol) were dissolved in 10 ml of dimethylsulfoxide and heated at 65 °C. After 1 h, 3-(chloromethyl)-3-methyloxetane (3.19 g, 26.5 mmol) was added to the reaction mixture dropwise. The reaction flask was heated at 65 °C for 72 h. The mixture was cooled and dichloromethane and de-ionized water were added; the aqueous phase was separated and washed with dichloromethane. The combined organic layers were washed twice with water and dried over magnesium sulfate. Removal of solvent by rotary evaporator yielded a viscous oil which solidified upon standing. The solid was triturated in hot ethanol and was allowed to cool overnight. The mixture was filtered to give a fine white solid pure 2-Ox (2.133 g). Yield=48%. ¹H-NMR (300 MHz, CDCl₃) δ (ppm), 7.76 (*d*, 2H), 7.38 (*d*, 2H), 7.35 (*t*, 2H), 7.26 (*t*, 2H), 7.13 (*d*, 2H), 6.78 (*d*, 2H), 4.60 (*d*, 4H), 4.43 (*d*, 4H), 3.96 (*s*, 4H), and 1.40 (*s*, 6H).

Resist solutions were made by dissolving 2-Ep or 2-Ox with 5.0 mol % (relative to total solids) triphenylsulfonium hexafluoroantimonate into cyclohexanone and filtering the solution through 0.2 μm polytetrafluoroethylene filters. The solutions were spin coated to form films that received a postapply bake (PAB) of 90 °C for 120 s. After e-beam exposure, the films were given a postexposure bake (PEB) of 90 °C for 60 s. The DUV exposures received a variable temperature PEB for 60 s as will be specified later. Development was carried out using puddle development in methyl isobutyl ketone (MIBK) for 30 s followed by a rinse with isopropyl alcohol and dried using nitrogen. No additional additives

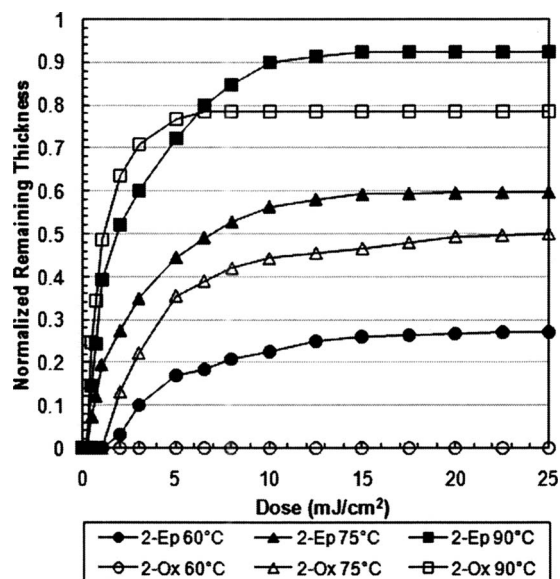


FIG. 2. DUV (248 nm) contrast curves for 2-Ep and 2-Ox at different PEB temperatures at a constant time of 60 s followed by development in MIBK.

such as quenchers were used in these formulations. Unexposed film thicknesses for DUV contrast curves and e-beam patterning were approximately 70 nm.

III. RESULTS AND DISCUSSION

Qualitatively, both 2-Ep and 2-Ox showed promising behavior during the initial testing. Both materials formed good quality amorphous films by spin casting and showed no dewetting on unprimed silicon wafers during either spin casting or baking at the temperatures required for the PAB or PEB. This ability to form high quality stable films is improved relative to some other recently reported epoxide functionalized molecular resists.²² Additionally, no film thickness change was observed after either exposure or PEB, which is consistent with the expectation that there would be essentially no formation of volatile products during imaging and that the cationic ring-opening polymerization used in these materials should result in very little shrinkage.²⁶ This result is promising in terms of any potential resists formulated with these materials passing the stringent outgassing requirements for EUV patterning. The low shrinkage in the material should prevent any stress buildup in the imaged features that might lead to pattern distortion after development. Finally, the unexposed resist film in both materials cleanly dissolves in MIBK very rapidly with no measurable scumming.

The DUV contrast curves for 2-Ep and 2-Ox for different PEB temperatures are shown in Fig. 2. All of these curves were made at a constant PEB time of 60 s and development time of 30 s in pure MIBK. The contrast curves generally all have a similar shape, with the thickness increasing linearly with dose at low doses followed by a transition to a plateau region at higher doses. At a PEB temperature of 60 °C, no film remains after development for 2-Ox indicating that the polymerization of the oxetane material never proceeded to a point sufficient to generate insoluble polymer species. For

2-Ep, a PEB temperature of 60 °C is sufficient to obtain some polymers and networks with a molecular weight sufficiently high to become insoluble (or at least dissolve so slowly that they do not dissolve in the allotted development time) in the developer. However, at this low bake temperature there is a significant thickness loss in the 2-Ep material due to the nominally non-networked and low molecular weight material that is dissolved during development. At 75 °C, both resists show somewhat similar behavior, with the oxetane polymerization showing the production of insoluble material at a higher dose than the 2-Ep epoxide polymerization. The minimal dose for any remaining film thickness to be observed in 2-Ep is approximately 0.5 mJ/cm², while in 2-Ox this minimal dose is in the range of 1–2 mJ/cm². At high doses, 2-Ep shows slightly larger remaining film thickness as compared to 2-Ox. Increasing the PEB temperature to 90 °C, the polymerization rate at low dose for 2-Ox finally exceeds that of 2-Ep as indicated by the higher remaining film thickness for 2-Ox as compared to 2-Ep in the linear low dose region for any given exposure dose. However, in the case of the 90 °C PEB, the 2-Ox still has less remaining film thickness than 2-Ep in the high dose plateau region. This indicates that the 2-Ox system still reaches a lower limiting conversion of the 2-Ox monomer than 2-Ep at these higher PEB temperatures even though the initial polymerization rate of 2-Ox appears to be higher under these conditions.

The linear region at low doses is due to a kinetically controlled polymerization reaction. The extent of polymerization increases linearly with initiator concentration (i.e., photoacid) for a fixed polymerization time (i.e., for a fixed PEB time) since the total conversion of monomer into polymer is only controlled by the number of active polymerization centers. The plateau region at higher doses occurs because the polymerization becomes diffusion controlled. The polymerization becomes diffusion controlled because the cross-linked network has significantly less mobility than the initial small monomer molecules and the photoacids. This reduction in mobility makes it hard for the network to grow larger and restricts the mobility of all molecules in the matrix as the polymerization proceeds. Since the surrounding molecules are restricted, increasing the amount of initiator (i.e., increasing the dose and producing more photoacid) does little to further increase cross-linking. This behavior has been observed in numerous other solid state cross-linking systems, and spectroscopic studies confirm that epoxide and oxetane conversion plateaus give rise to the plateau in film thickness.²⁷ Increasing the PEB temperature gives the film more mobility, allowing further cross-linking and higher monomer conversion into the polymer and polymer network, thus resulting in a larger maximum remaining film thickness after development.

Studies of polymerizations of epoxides and oxetanes using photo-differential scanning calorimetry and Fourier transform infrared spectroscopy in literature show that epoxides generally have faster initiation (i.e., the initial attack of an acid protonated monomer ring by another monomer

ring that starts the polymerization propagation process) rates than oxetanes while oxetanes have faster propagation (i.e., the addition and reaction of new reactive bonds to the growing polymer chain) rates than epoxides.²⁴ It has also been reported that the propagation rates of oxetanes are much faster than their initiation rates.²⁸ This is consistent with the results seen for 2-Ep and 2-Ox. At 60 °C, there is not enough thermal energy to activate a significant amount of initiation in 2-Ox, and so at even at high photoacid initiator concentrations (i.e., high dose) there is little polymerization. At 75 °C, the minimal dose for any remaining film thickness is higher for 2-Ox compared to 2-Ep, indicating that more photoacid (i.e., initiator) is required for 2-Ox, but 2-Ox has a slightly higher slope in the contrast curve than 2-Ep in the linear low dose region due to the faster propagation of the oxetane. For the PEB at 90 °C, 2-Ox shows a much sharper initial slope in the contrast curve than 2-Ep, which is again due to the faster propagation rate of the oxetane.

The differences in the initiation and propagation rates of each functional group could also explain the difference in the maximum final film thickness observed for each resist at a given bake temperature. Since 2-Ox has a faster propagation rate than the initiation rate, the final network structure of the cross-linked 2-Ox resist will be very different than in the case of 2-Ep which has a faster initiation and slower propagation than 2-Ox. Comparing 2-Ep and 2-Ox polymerizations, polymerization and cross-linking of 2-Ep are probably best thought of as many small slowly growing chains that relatively suddenly form an extensive network at high monomer conversion. Polymerization and cross-linking of 2-Ox are better thought of as significantly fewer initiated chains that incorporate monomer at a much faster rate than in the case of 2-Ep. This fast propagation of a smaller number of polymerizing sites leads to longer linear chains that eventually form a network in 2-Ox. A diagram demonstrating the differences in the network formation and structure for oxetanes and epoxides is shown in Fig. 3. Figures 3(a) and 3(d) show the initiated sites for epoxides and oxetanes, respectively; since the rate of initiation is higher in epoxides, it has more initiated sites. Figures 3(b) and 3(e) show each type of functional group after propagation before network formation; the oxetane has longer chains because it has a faster rate of propagation. Figures 3(c) and 3(f) show the final network; while they both have formed fully cross-linked networks, the epoxide has a much more dense network with more molecules incorporated into the network. 2-Ep likely has a heavily cross-linked network with relatively short distances between cross-links while 2-Ox forms a network that has much longer distances between cross-links. This difference in the length of the polymer chains between cross-links will have a direct impact on the swelling behavior of these materials. Also, due to these differences in initiation rate versus polymerization rate, the maximum extent of monomer conversion (i.e., polymerization) at a given PEB temperature could also be very different in these two materials. This explains the larger thickness loss at high doses in the case of 2-Ox as compared to 2-Ep for a given bake temperature.

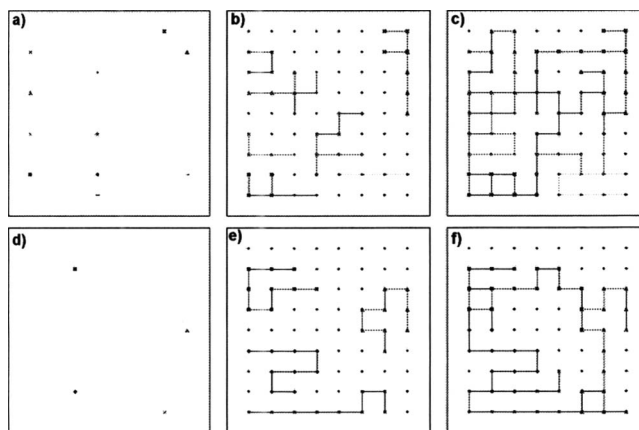


FIG. 3. Diagram demonstrating differences in polymerization and network formation in epoxide and oxetane resists: (a) epoxide initiation, (b) epoxide propagation, (c) epoxide network, (d) oxetane initiation, (e) oxetane propagation, and (f) oxetane network. Points in (b), (c), (e), and (f) are nonpolymerized molecules and are omitted in (a) and (d) for clarity.

High resolution patterning of 2-Ep and 2-Ox was carried out using 100 keV e-beam lithography. For 2-Ep, a dose of $75 \mu\text{C}/\text{cm}^2$ was patterned at the correct nominal size for most features. Figure 4 shows the SEM of e-beam patterning of 2-Ep for 50, 30, and 25 nm 1:1 line/space patterns and 20 nm 1:2 line/space patterns. Patterns are resolved down to 25 nm 1:1 in 2-Ep with no added quencher or other polymerization control agent. The 20 nm 1:2 line/space patterns are resolved, but the lines are slightly wider than 20 nm which is likely due to the propagation of polymerization beyond the nominally exposed region (i.e., the equivalent in these negative tone cross-linking materials of photoacid diffusion induced blur seen in positive tone CARs). The 20 nm 1:1 line/space patterns are intact but do not cleanly clear at some points. Despite the fact that there is some blur in these materials, it is reduced compared to conventional photoacid catalyzed positive tone resists since 2-Ep can well resolve 25 nm half-pitch with no additional polymerization or diffusion control agent. Also interestingly, 2-Ep still obtains very low LER while providing excellent resolution and sensitivity. For 50 nm half-pitch lines, the LER (3σ) was 2.8 nm and the LWR (3σ) was 4.0 nm. The 30 nm half-pitch lines obtained LER (3σ) of 2.9 nm and LWR (3σ) of 4.2 nm. This is a

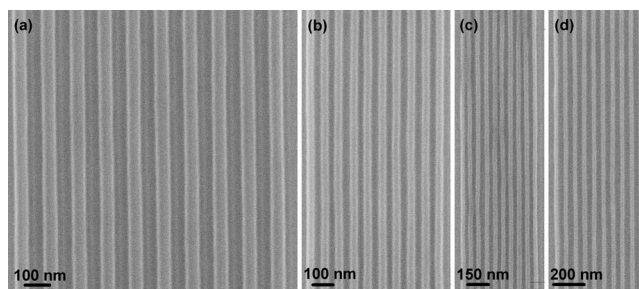


FIG. 4. SEM of e-beam (100 keV) patterning of 2-Ep with a PEB of 90 °C (a) 50 nm 1:1 line/space, (b) 30 nm 1:1 line/space, (c) 25 nm 1:1 line/space, and (d) 20 nm 1:2 line/space.

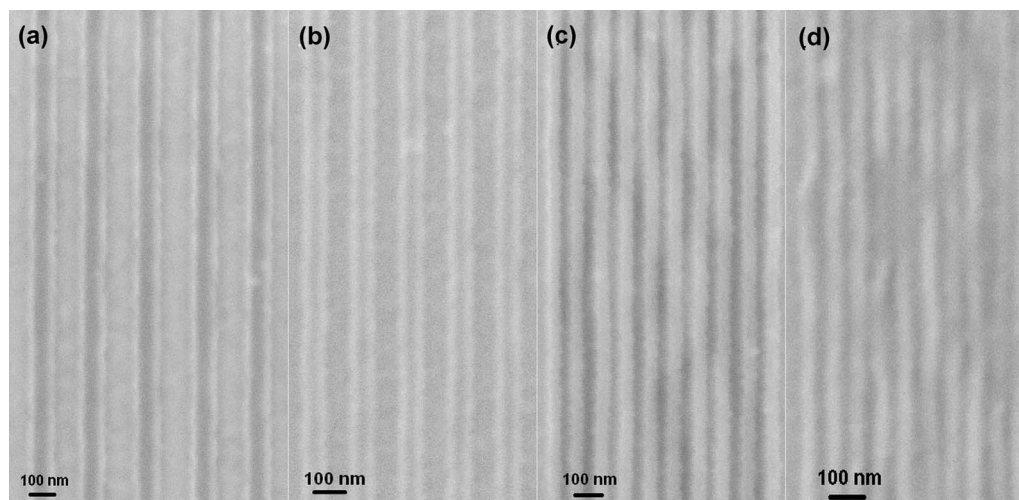


FIG. 5. SEM of e-beam (100 keV) patterning of 2-Ox with a PEB of 90 °C: (a) 100 nm 1:1 line/space, (b) 70 nm 1:1 line/space, (c) 50 nm 1:1 line/space, and (d) 45 nm 1:1 line/space.

significant improvement compared to most other resists that have reported LER (3σ) values in the range of 4–6 nm.

The SEM results of the e-beam patterning of 2-Ox are shown in Fig. 5 for 100 nm 1:1 line/space, 70 nm 1:1 line/space, 50 nm 1:1 line/space, and 45 nm 1:1 line/space patterns exposed at a dose of $75 \mu\text{C}/\text{cm}^2$ at 100 keV. The material resolves well down to 50 nm half-pitch but has limited resolution below 50 nm where it appears to fail due to line blur and swelling. As can be seen in the 45 nm patterns, there are multiple points where the lines appear to be stuck together and there are other places where the line does not hold its shape (e.g., along the left edge). The distortion observed in these smaller features in 2-Ox is likely due to swelling. 2-Ox also clearly shows some blurring, i.e., polymerization outside of the nominally exposed regions. This is visible if one compares the measured versus nominal size of line features at a given dose. As the nominal line size decreases, the relative error in the line size increases. The nominally 70 nm lines are correctly sized at 1:1 line spacing, but the nominally 50 nm lines are wider than the spaces. This effect is likely due to the blurring of the pattern edge by propagation of polymerization beyond the line edge as a result of the fast propagation reactions in 2-Ox. Such propagation outside the nominally exposed region would likely occur over a similar length scale away from the printed line edge regardless of the size of the line itself, and this would cause a more significant sizing error as the nominal line size decreases as observed in the e-beam imaging data from 2-Ox. The LER performance of 2-Ox is also clearly not as good as 2-Ep, with 2-Ox at 70 nm 1:1 line features exhibiting a LER (3σ) of 10.0 nm and a LWR (3σ) of 14.1 nm.

The high resolution imaging data support the earlier discussion on the mechanistic and kinetic effects in the cross-linking of 2-Ep and 2-Ox. These types of resists are able to obtain good resolution (excellent resolution for 2-Ep) with no added polymerization control agent (e.g., such as a base quencher) because their imaging mechanism is based on cationic polymerization which is different from that of conven-

tional acid catalyzed deprotection based resists. Since the active species in these resists is an ionic active site which is attached to the end of an ever growing polymer chain or network, its mobility is intrinsically controlled. This is compared to a typical small molecule photoacid that can freely diffuse through a resist matrix. The swelling in these materials is reduced compared to larger polymers and oligomers likely because the initial unit is essentially a monomer.¹² Since the initial molecular resists are small molecules, the unexposed areas between lines rapidly dissolve to open spaces before catastrophic swelling can occur. Likewise, since the initial resist units are so small, extensive cross-linking must occur to render the resist insoluble in the developer. This extensive cross-linking leads to the relatively low swelling compared to polymer negative tone resists.¹² Although these materials swell less than polymers, swelling can still be an important issue in these materials. Swelling appears to be a primary reason that causes 2-Ox to perform more poorly than 2-Ep. In epoxide polymerization, since the rate of initiation is comparable to or faster than that of propagation, the final network structure has a high density of cross-links, as described earlier and as shown in Fig. 3(c). While this does not guarantee elimination of swelling, it reduces it enough to allow very high resolution. Since the oxetane polymerization has much faster propagation than initiation, the final network should have a lower density of cross-links as seen in Fig. 3(f). This less dense network can imbibe more solvent and thereby swell to a greater extent than the epoxide network, thus limiting the resolution of 2-Ox. The higher propagation rate of oxetanes could also lead to more blur outside the exposed region as is seen in 2-Ox. Another potential issue with oxetanes as polymerizable groups for negative tone resists is again due to the low initiation rate of the polymerization. Since oxetane initiation is slow, it has been shown that ring protonation by the photoacid in oxetane is reversible,²⁹ meaning that free photoacid can likely exist during patterning of an oxetane functionalized resist. This could potentially provide another explana-

tion for the greater blur and LER in 2-Ox compared to 2-Ep, where the photoacid is almost immediately consumed by initiation of the polymerization.

IV. CONCLUSIONS

Epoxide (2-Ep) and oxetane (2-Ox) functionalized molecular resists with identical cores were synthesized to compare the effect of each functional group in high resolution patterning of negative tone molecular resists. Both resists had a good sensitivity of $75 \mu\text{C}/\text{cm}^2$ under 100 keV e-beam patterning on electron transparent Si_3N_4 thin membrane substrates. The epoxide resist had excellent resolution of sub-25-nm half-pitch with low LER (3σ) of 2.9 nm, while the oxetane resist was only able to obtain 50 nm half-pitch with a worse LER (3σ) of 10.0 nm. The differences in the resist performance are attributed to the differences in the kinetics of the cationic polymerization of each group. The fast initiation and slow propagation of the epoxide polymerization lead to a high density network which allows for high resolution through reduced blur and swelling. The oxetane polymerization, which has fast propagation and slow initiation, leads to a lower density network that has reduced resolution due to increased blur and swelling. Epoxide functionalized resists show promise as potential candidates for future generations of high resolution e-beam and EUV patterning due to their favorable combination of resolution, sensitivity, and line edge roughness. In contrast, oxetane functionalized materials appear to be less useful (at least as pure resins) in formulating high resolution molecular resists.

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